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Macromolecular smart materials and structures were designed and characterized. The designs were based on oligomeric modules, each of which is responsible for a particular function in the smart material, or in the structure of which it is a part. Liquid crystals and block copolymers were also characterized for potential use as modules. Computer modeling of molecular architecture and motion was used to identify oligomers that can provide useful functions in a smart molecule system. Networks of oligomers, polymers, and block copolymers with well defined structures were identified and synthesized. Functional groups at specific locations were used to create the networks. Molecular scale assemblies were attached to mica or graphite and observed by atomic force microscopy or scanning tunneling microscopy. Rubbery networks containing strain sensitive chromophores were characterized by optical spectroscopy.

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Functions performed by the various oligomers that were examined include attachment of the oligomer to a graphite or mica surface, incorporation of a chromophore into an elastomeric network, piezochromic effects, formation of bonds that can be broken predictably by forces that do not break the backbone chain, and maintenance of a force transmitting connection between a reinforcing fiber and the polymer matrix in the presence of high strain.

Potential applications of the results of this project include health monitoring of composite structures such as aircraft and land vehicles. The work is highly innovative and the implications are far reaching. This work is an example of a powerful approach to design of materials that are both new and smart. Oligomers that are sensitive to strain, stress, incident photons, certain small molecules, electric fields, or hydrostatic pressure in networks can be combined with structures that provide other smart material functions such as signal transmission, signal processing, or actuation of useful changes.

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Final Technical Report

SMART MATERIALS BASED UPON OLIGOMERIC MOLECULES

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Maurice Morton Institute of Polymer Science
The University of Akron

March 15, 1991 to April 15, 1994
and
Annual Report for 1993

BRIEF OUTLINE OF RESEARCH FINDINGS

Introduction:

Macromolecular smart materials and structures were designed and characterized. The designs were based on oligomeric modules, each of which is responsible for a particular function in the smart material, or in the structure of which it is a part. Liquid crystals and block copolymers were also characterized for potential use as modules. Computer modeling of molecular architecture and motion was used to identify oligomers that can provide useful functions in a smart molecule system. Networks of oligomers, polymers, and block copolymers with well defined structures were identified and synthesized. Functional groups at specific locations were used to create the networks. Molecular scale assemblies were attached to mica or graphite and observed by atomic force microscopy or scanning tunneling microscopy. Rubbery networks containing strain sensitive chromophores were characterized by optical spectroscopy.

Functions performed by the various oligomers that were examined include attachment of the oligomer to a graphite or mica surface, incorporation of a chromophore into an elastomeric network, piezochromic effects, formation of bonds that can be broken predictably by forces that do not break the backbone chain, and maintenance of a force transmitting connection between a reinforcing fiber and the polymer matrix in the presence of high strain.

Potential applications of the results of this project include health monitoring of composite structures such as aircraft and land vehicles. The work is highly innovative and the implications are far reaching. This work is an example of a powerful approach to design of materials that are both new and smart. Oligomers that are sensitive to strain, stress, incident photons, certain small molecules, electric fields, or hydrostatic pressure in networks can be combined with structures that provide other smart material functions such as signal transmission, signal processing, or actuation of useful changes.

Strain sensitive smart material:
We successfully designed, synthesized and tested a smart material that preserves a record of the maximum amount of mechanical strain that the material has ever experienced.[1,2]

This smart material combines a strain sensitive chromophore (cis-azobenzene), a nylon based system of hydrogen bonds that latch the azobenzene in the cis form, and attachments to a polyurethane elastomer to apply stress to the ends of the nylon segments. The force breaks the hydrogen bonds and helps the azobenzene to transform to the trans conformation, which has a strong ultraviolet absorption band.

Figure 3. Strain sensitive smart molecule, before stretching (top), and at the maximum stretch (bottom).
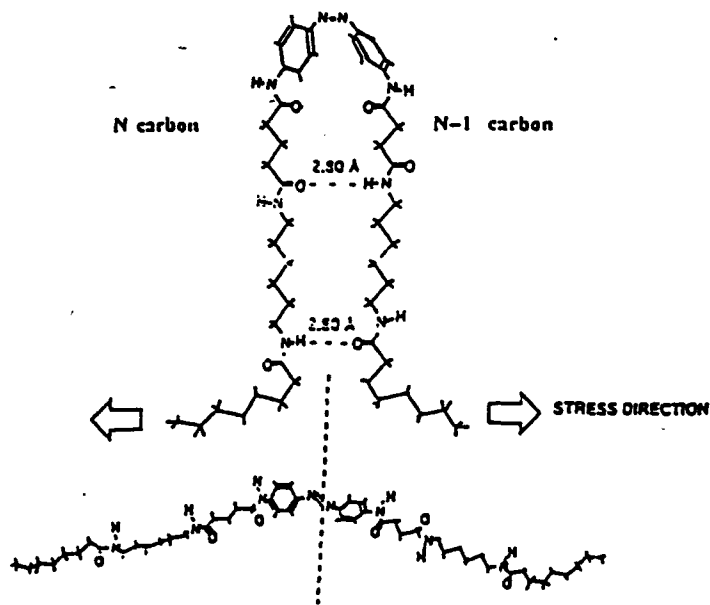
Figure 3 shows the structure of the molecule and, in a schematic way, its behavior. Figure 4 shows the increase in the number of trans-azobenzene molecules as the material is stretched three times to 100% elongation and relaxed, then stretched three times to 200% and relaxed and finally stretched three times to 300% and relaxed. The increase in the number of trans-azobenzene molecules in successive stretches was relatively small until the strain exceeded the previous maximum strain, and then many cis-azobenzenes were transformed. The material was recycled to a state with mostly cis-azobenzenes by heating to about 100° C and irradiating with ultraviolet light. It then responded to a second cycle of stretching in essentially the same way as it did to the first. No primary bonds are broken in the material. Its ultimate load bearing capacity is not affected by repeated cycles of use.
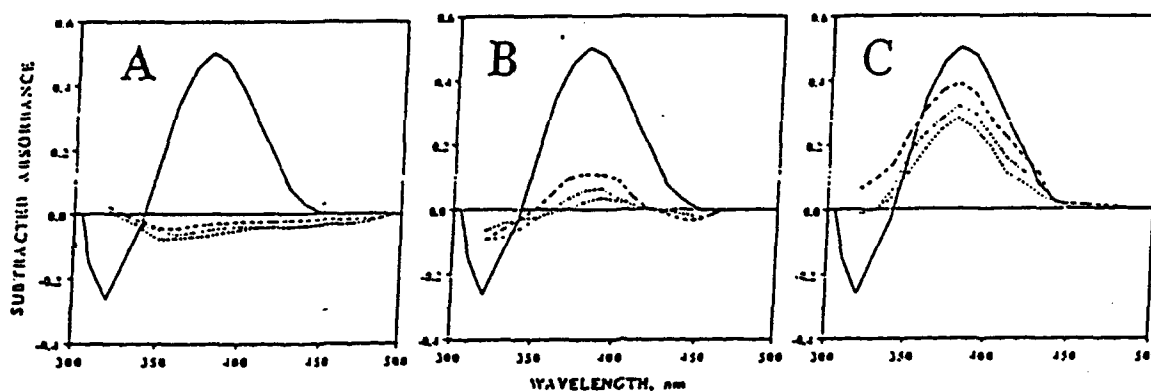

Figure 4. Increase in the number of trans bonds caused by 3 successive stretches to (A) 100%; (B) 200%, (C) 300% elongation.

These results demonstrate that such a complicated smart material can be successfully designed, synthesized and tested. The use of the hydrogen bonds on a polymer as weak links to latch a molecule in a desired conformational state is expected to be generally useful. The use of an elastomer network (in this example, polyurethane) as a "test bed" to apply forces along the chain axis likely to be useful in a number of other investigations of the response of molecules to tensile forces applied through chemical bonds.

Smart materials based on polydiacetylene segmented block copolymers:
Polyurethane segmented block copolymers were prepared using polydiacetylene hard segments and polybutadiene soft segments. The soft phase segments were formed by the reaction of well-defined hydroxy- and dihydroxy-functionalized polybutadienes with two equivalents of 4,4'-methylene bis(phenylisocyanate) (MDI) to form the corresponding telechelic isocyanate-functionalized polybutadienes. The segmented polyurethanes were prepared by coupling this telechelic di-isocyanate with the diacetylene, 2,4-hexadiyne-1,6-diol, as shown in Scheme 3. The resulting segmented block copolymers undergo cross-polymerization of the diacetylene units to form a blue-colored polydiacetylene hard phase upon either heating or photolysis. The sensitivity to heat could be utilized as a sensor, since cross-polymerization of the initially formed, colorless segmented polyurethane to form a blue polymer occurs upon heating. The color of these materials is dependent on the conjugation length of the polydiacetylene, which subsequently (i.e., after cross-polymerization) can be changed by heating or application of stress after cross-polymerization. This segmented polymer also undergoes reversible thermochromic shifts when heated below 180° C, and an irreversible color change from blue to red upon heating above 180° C. Wide-angle X-ray

scattering analysis indicates that the polydiacetylene phase crystalline interferences at a Bragg angle of 9.3 degrees are lost at 180° C. Thus, a considerable range of application as thermochromic sensors is provided by a combination of the initially formed polymer (colorless), and the cross-polymerized polymer (blue) and the polymer heated above 180° C (red).

The thermogravimetric anaysis of these cross-polymerized, segmented block copolymers indicates that they exhibit better thermal stability than the corresponding polyether-based polyurethanes. Both dynamic-mechanical-temperature analysis and differential thermal analysis clearly support the conclusion that these polyurethanes (20% hard segment content) exhibit two phases, a rubbery polybutadiene phase (transition below -50° C) and a crystalline hard domain (transitions at 135 to 145° C) characterized by an X-ray Bragg angle of 9.3 degrees. Above the hard domain transition, only an amorphous halo is observed in the X-ray diffraction pattern, indicating the loss of crystalline order.

Stress-strain studies interpreted using the Mooney-Rivlin relationship showed that the high deformation tensile modulus of the segmented polyurethane increases from 0.97 N/mm^2 before cross-polymerization to 1.47 N/mm^2 after cross-polymerization. This modulus also increased at higher elongations for the cross-polymerized sample compared to a decrease observed for samples before cross-polymerization. The Young's modulus increased from 5.6 to 7.8 N/mm^2 upon cross-polymerization.

The mechanochromic properties of a cross-polymerized segmented block copolymer were briefly investigated by elongation of the samples in the sample compartment of a UV-visible spectrophotometer. The absorption maximum shifted reversibly to shorter wavelengths upon elongation.

In conclusion, these segmented polyurethane block copolymers based on a polybutadiene soft phase and a polydiacetylene hard phase have potential as useful thermochromic and mechanochromic sensors. The stress-strain properties of these polymers can be varied systematically by changing the molecular weight of the rubbery block and also by varying the proportion of the hard phase.

Scheme 3.
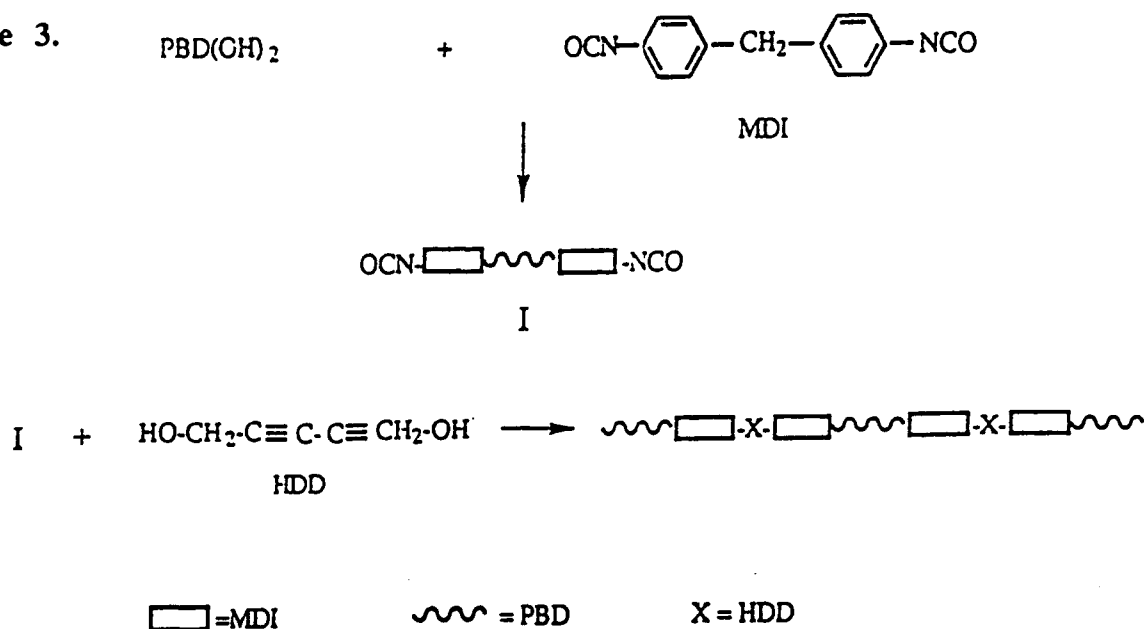
Microphase separation in block copolymers:

Figure 2. An image of a calculated arrangement of a polybutadiene molecule at a density of 0.89 g/cm^3. The edge of the box is about 2.1 nm long.[3]
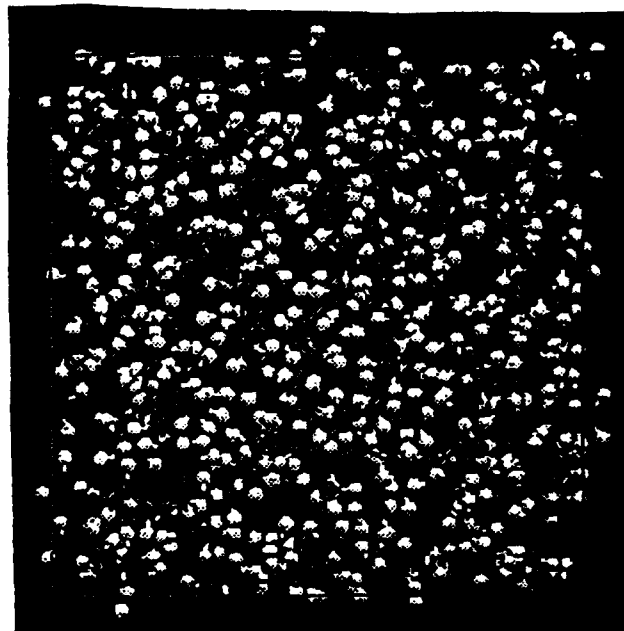
One of the most important larger scale organizations of synthetic polymers is the separation of the different blocks into two distinct phases. Block copolymers are used as the basis for moldable elastomers in which a rigid phase serves as crosslinks between elastomeric molecules, memory materials such as heat shrinkable tubing, and for compatibilization of polymer blends. These commercial applications of block copolymers can be viewed as important steps toward the creation of smart materials.

The presence of soft and hard blocks in polymer chains promotes formation of microphases with supermolecular organization as a result of selective segregation of the blocks, driven by their incompatibility. Depending upon composition, chemical structure of the blocks, molecular weight, presence of a third component such as a selective solvent, a variety of microphase morphologies can occur.

Recently simulations have been developed in which diblock copolymers at high density are seen to spontaneously self-assemble into a variety of structures: spheres, cylinders, OBDD, or lamella.[4] The transitio from the disordered phase to lamellae has been studied in detail in symmetric diblock copolymers,[5] and the anisotropy of the self-diffusion coefficient has been evaluated for the chains in the lamellar state.[6] These simulations will be adapted to systems that contain triblock copolymers pertinent to the present proposal.

The crucial parameter governing block segregation is the length of the block, N and the value of the interaction parameter χN, for diblock polymers with flexible segments, three regions on the phase diagram are interesting: a homogeneous state with a random mixture of blocks near $\chi N \cong 0$; a weak segregation region with a weak modulation of density and composition, with extended interface zones for χN between 1 and 10; and a segregation region for higher χN. Definite microphase structures occur, such as cubic, cylindrical, inverted cubic and inverted cylindrical, depending upon the composition of the block copolymers. While not all aspects of the formation of microphases are known, for flexible polymers with 2 or 3 different kinds of blocks, some trends and relationships are well understood.

In contrast, in systems such as multiblock polymer or block copolymers containing one hard segment, the relationships that govern formation of microphase structures are not clear from either

a theoretical or experimental point of view. The tendency to form lamellar and nematic liquid-crystalline (LC) like phases for di-block polymers with one hard segment was examined theoretically and the role of microphase separation of soft and hard segments in the formation of LC structures was observed experimentally. Even from these very restricted data, it is apparent that there is a strong tendency for segregation and formation of ordered, mesomorphic microphase structures in systems with a content of hard blocks of more than 10 or 20%. Cooperative effects leading to orientation of the hard segment domains in a LC phase may be beneficial, if they lead to better coupling with the external electric field.

Another possibility in phase separated block copolymer systems is the dilution of the hard block phase by addition of a selective solvent which will solvate only this phase. The addition of a selective solvent at a volume concentration of 50 to 70% sometimes leads to the formation of soft materials as the concentration of the hard blocks approaches the dilute regime. In such domains, for intermediate solvent concentration, various lyotropic mesomorphic structures with high mobility in the ordered regions can form. This opens the possibility for reorientation motions of the hard segments in which is effectively a lyotropic state. A few crosslinks between the polymer backbones can provide enough elastomeric behavior in sme multicomponent systems to maintain the macroscopic shape without disturbing desirable organization in the microphase.

Morphology of liquid crystals and other organized molecular systems: The surfaces of several kinds of ordered molecular systems which are candidates for use in smart material systems were examined by atomic force microscopy. Monolayer films from discotic liquid crystals showed periodic features of the ordered molecules.[7] The surface morphology of cyanine dye single crystal sheets grown on lipid monolayers was observed.[8] Langmuir-Blodgett films from ladder polyheteroarylenes,[9] from polyglutamate[10,11] and multilayer films[12] were also characterized. In many cases, the mechanical properties of the films were examined by using the atomic force tip to scrape holes in the films.

Calculation of electronic properties of diacetylene and azobenzene containing molecules subjected to molecular distortions. Quantum mechanical calculations of the changes in the electronic states of polymer molecues were made[13,14] for molecules which were subjected to tension, to bending, or to twist which induced cis-trans isomerization of the azobenzene molecules. The relationships between the deformation and shifts in the electronic states were observed.

Attachment to carbon black or to graphite: As a part of our study of the attachment of oligomers to graphite, we observed[15] the morphology of carbon black particles. The scanning tunneling microscope showed the greatest detail of the sufaces of the carbon black particles. Hexagonal arrays of individual carbon atoms were resolved on many of the facets of graphitized medium thermal carbon black. These morphological features had never been observed before. Other kinds of carbon black had surfaces with very complicated morphology that contained many ledges and crevices long which a polymer could lie. The transmission electron microscope showed internal structure and the scanning electron microscope showed the overall structure of the particle aggregates. The attachment of polyimides and Nylon 6/6 to graphite[16] was observed. Other aspects of surface morphology were examined by scanning tunneling and atomic force microscopy.[17,18,19]

Trans-cis isomerization of stilbene in a polybutadiene oligomer: Molecular dynamics methods were used to model the photoinduced trans-cis isomerization of stilbene. The presence of the attached polybutadiene increases the activation energy of the transition. The changes in the positions of the atoms in the polybutadiene chains caused by the transition extend about 2 nm from the stilbene. It is likely that a relatively simple functional expression of the average changes in position can be obtained and the parameters in the function determined from the results of the

molecular dynamics calculation. This analysis provides information of the type needed to predict the "reset", or "initialization" behavior of a smart molecule in which the cis form of a stilbene is created by UV irradiation.

Molecular Dynamics calculations: Results from molecular dynamics calculations of rubbery oligomers of polybutadiene are described and resulting publications referred to in the section above called "Design of Elastomer with Dipoles".

We have published the descriptions of fully atomistic models for amorphous polybutadiene with four microstructures: 1,4-cis,[20] 1,4-trans,[21] vinyl, and a mixed structure composed of 55% trans, 35% cis, and 10% vinyl, all at a density of 0.89 g/cm^3. Figure 2 depicts the arrangement of the chains in one of these models. We have analyzed the manner in which the distribution of free volume depends on the microstructure,[22] and are currently studying the molecular dynamics of the amorphous systems at bulk density.[23,24,25] These models can be analyzed to investigate the storage of strain energy in the elastomer, and the transmission of forces through the elastomer for real polymer molecules. This information is needed to optimize the choice of length and molecular nature of the elastomer.

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